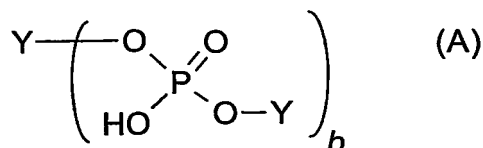


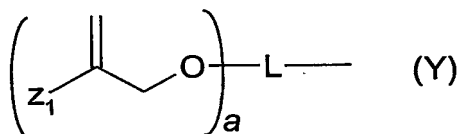
## Claims

1. One-part self-etching, self-priming dental adhesive composition having a pH of at most 2, which comprises
- (a) a polymerizable acidic phosphoric acid ester monomer of the following formula (A):



wherein

the moieties Y independent from each other represent a hydrogen atom or a moiety of the following formula (Y)



wherein

$Z_1$  is  $\text{COOR}^{10}$ ,  $\text{COSR}^{20}$ ,  $\text{CON}(\text{R}^{10})_2$ ,  $\text{CONR}^{10}\text{R}^{20}$ , or  $\text{CONHR}^{10}$ , wherein  $\text{R}^{10}$  and  $\text{R}^{20}$  independently represent

a hydrogen atom,

a  $\text{C}_{1-18}$  alkyl group optionally substituted by a  $\text{C}_{3-8}$  cycloalkyl group,

an optionally substituted  $\text{C}_{3-8}$  cycloalkyl group,

an optionally substituted  $\text{C}_{4-18}$  aryl or heteroaryl group,

an optionally substituted  $\text{C}_{5-18}$  alkylaryl or alkylheteroaryl group, or

an optionally substituted  $\text{C}_{7-30}$  aralkyl group,

whereby two  $\text{R}_1$  residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

and whereby the optionally substituted groups may be substituted by 1 to 5  $\text{C}_{1-5}$  alkyl group(s);

L represents an  $(a+b)$ -valent organic residue (whereby b is 1 when Y in

formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including  $a + b$  carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said  $a + b$  carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

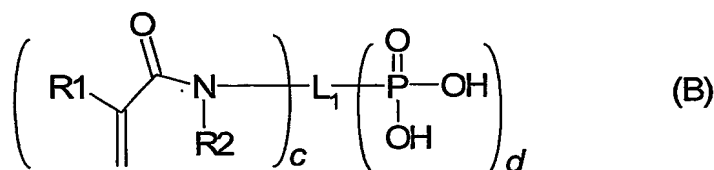
$a$  is an integer of from 1 to 10, preferably 1 to 5;

$b$  is an integer of from 1 to 10, preferably 1 to 5;

provided that at least one Y is not hydrogen; and

(b) one or more polymerisable acidic monomers selected from the group consisting of

(b1) polymerisable acidic monomers of the following formula (B):



wherein

$\text{R}_1$  and  $\text{R}_2$  independently represent

a hydrogen atom,

an optionally substituted  $\text{C}_{1-18}$  alkyl group,

an optionally substituted  $\text{C}_{3-18}$  cycloalkyl group,

an optionally substituted  $\text{C}_{5-18}$  aryl or heteroaryl group,

an optionally substituted  $\text{C}_{5-18}$  alkylaryl or alkylheteroaryl group,

an optionally substituted  $\text{C}_{7-30}$  aralkyl group,

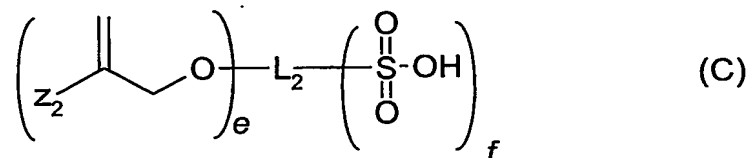
whereby the optionally substituted groups may be substituted by 1 to 5  $\text{C}_{1-5}$  alkyl group(s);

$\text{L}_1$  represents a  $(c + d)$  valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur, the carbon atoms including  $c + d$  carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said  $c + d$  carbon atoms linking a phosphonate or optionally substituted acrylamido group;

and

$c$  and  $d$  independently represent integers of from 1 to 10;

(b2) polymerisable acidic monomers of the following formula (C):

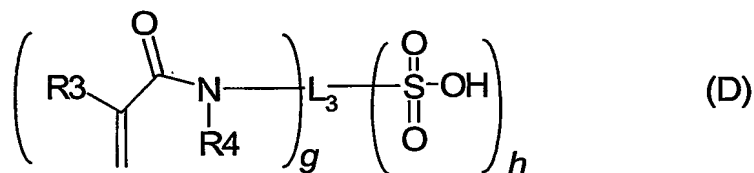


wherein

$\text{Z}_2$  independently has the same meaning as defined for  $\text{Z}_1$ ;

$\text{L}_2$  represents an  $(e + f)$  valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including  $e + f$  carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said  $e + f$  carbon atoms linking a sulphonate or optionally substituted 2-(oxa-ethyl)acryl derivative group; and  $e$  and  $f$  independently represent an integer of from 1 to 10;

(b3) acidic monomers of the following formula (D):



wherein

$\text{R}_3$  and  $\text{R}_4$  independently represent

a hydrogen atom,

an optionally substituted  $\text{C}_{1-18}$  alkyl group,

an optionally substituted  $\text{C}_{3-18}$  cycloalkyl group,

an optionally substituted  $\text{C}_{5-18}$  aryl or heteroaryl group,

an optionally substituted  $\text{C}_{5-18}$  alkylaryl or alkylheteroaryl group,

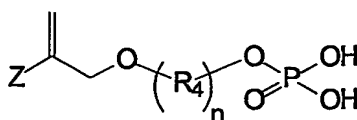
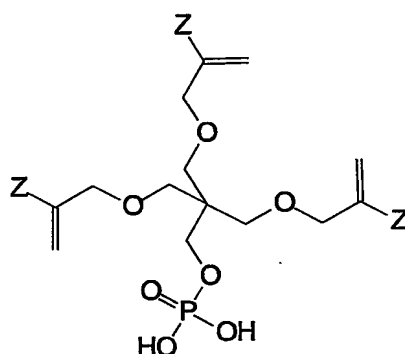
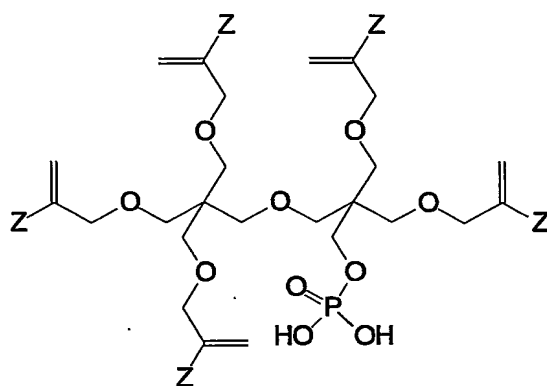
an optionally substituted  $\text{C}_{7-30}$  aralkyl group,

whereby the optionally substituted groups may be substituted by 1 to 5  $\text{C}_{1-5}$  alkyl group(s)

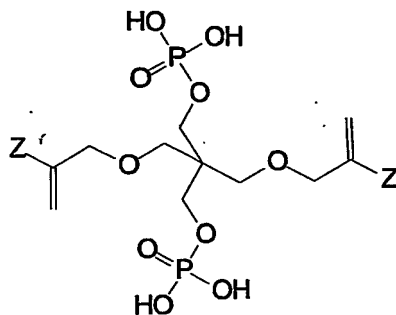
$L_3$  represents a ( $g + h$ ) valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including  $g + h$  carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said  $g+h$  carbon atoms linking a sulphonate or optionally substituted acrylamido group; and  $g$  and  $h$  independently represent integers of from 1 to 10;

- (c) a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer;
  - (d) optionally an organic and/or inorganic acid;
  - (e) an organic water soluble solvent and/or water; and
  - (f) polymerization initiator, inhibitor and stabilizer.
2. The one-part self-etching, self-priming dental adhesive composition of claim 1 wherein  $L_1$ ,  $L_2$ , and  $L_3$  independently represent an optionally substituted  $C_{1-18}$  alkylene group which may contain from 1 to 9 oxygen atoms in the chain, an optionally substituted  $C_{3-18}$  cycloalkylene group, an optionally substituted  $C_{5-18}$  arylene or heteroarylene group, an optionally substituted  $C_{5-18}$  alkylaryl or alkylheteroarylene group, an optionally substituted  $C_{7-30}$  aralkylene group.
3. The one-part self-etching, self-priming dental adhesive composition of claim 1 or 2 which is hydrolysis stable for at least one week at a storage temperature of 50 °C, whereby after such storage the bond strength of an adhesive prepared from such an adhesive composition to enamel and/or dentin is at least 10 MPa, preferably 15 MPa.
4. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein components (a) and (b) are contained in a ratio of from 1:100 to 100 : 1.
5. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said organic acid of component (d) is selected from the group of mono- or polycarboxylic acids such as methacrylic acid, acrylic acid, fumaric acid, maleic acid, citric acid, itaconic acid, formic acid and wherein the inorganic acid of component (d) is selected from the group of sulfonic acid, phosphoric acid, sulfuric acid and hydrofluoric acid.

6. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said organic water soluble solvent of component (e) is selected from the group of alcohols and ketones such as ethanol, propanol, butanol, acetone, methyl ethyl ketone.
7. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said acidic polymerizable monomer of component (a) is characterized by one of the following formulas:

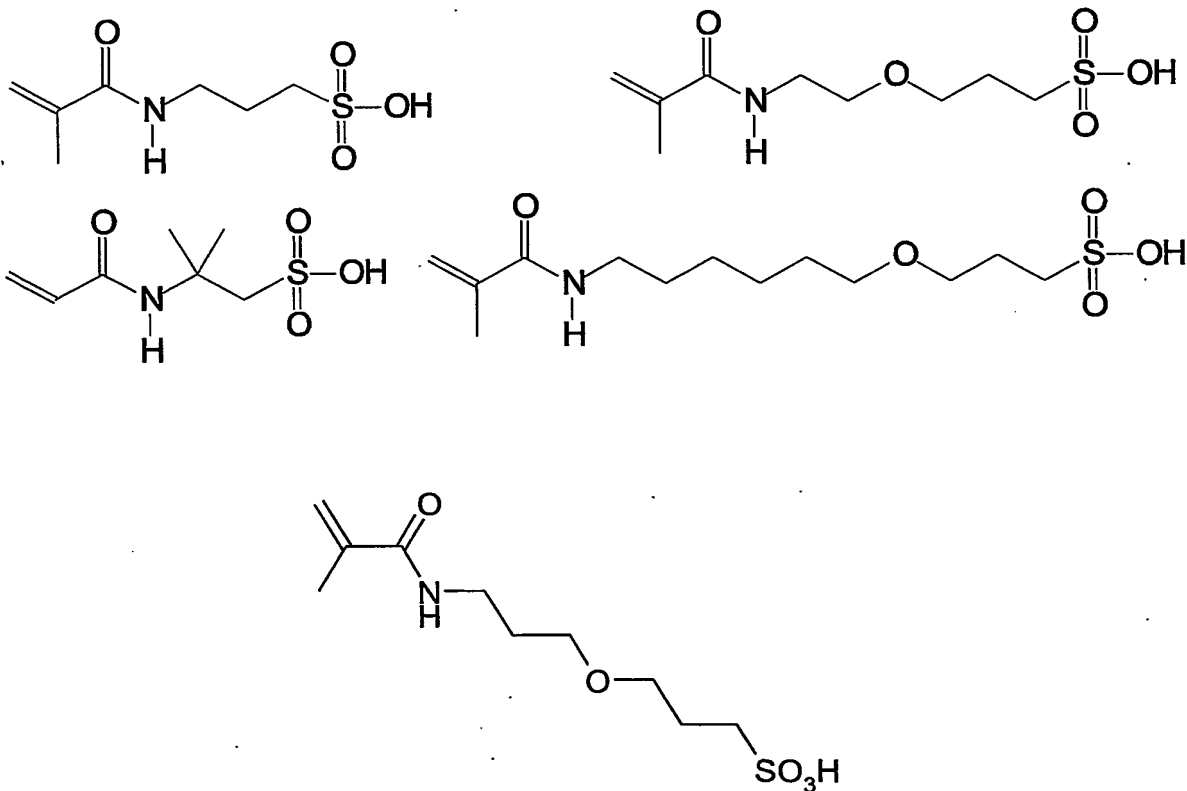


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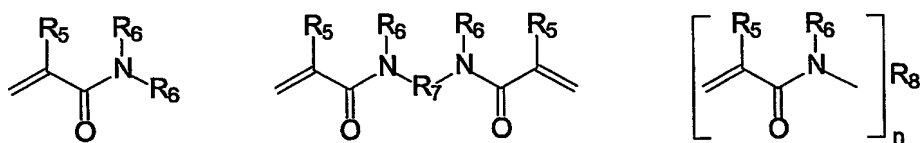


wherein Z is as defined in claim 1 and  
n is an integer.

8. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said acidic polymerizable monomer of component (b) is a polymerisable acidic monomers of formula (C).
9. Hydrolysis stable one-part self-etching, self-priming dental adhesive composition of claim 8, wherein said acidic polymerizable monomer is characterized by one of the following formulas:



10. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein the polymerizable N-substituted alkylacrylic or acrylic acid amide monomer of component (c) is characterized by one of the following formulas:



wherein

$R_5$  and  $R_6$  independently represent

- a hydrogen atom or a substituted
- a  $C_1$  to  $C_{18}$  alkyl group,
- an optionally substituted  $C_{3-18}$  cycloalkyl group,
- an optionally substituted  $C_{5-18}$  aryl or heteroaryl group,
- an optionally substituted  $C_{5-18}$  alkylaryl or alkylheteroaryl group,
- an optionally substituted  $C_{7-30}$  aralkyl group,

$R_7$  represents a

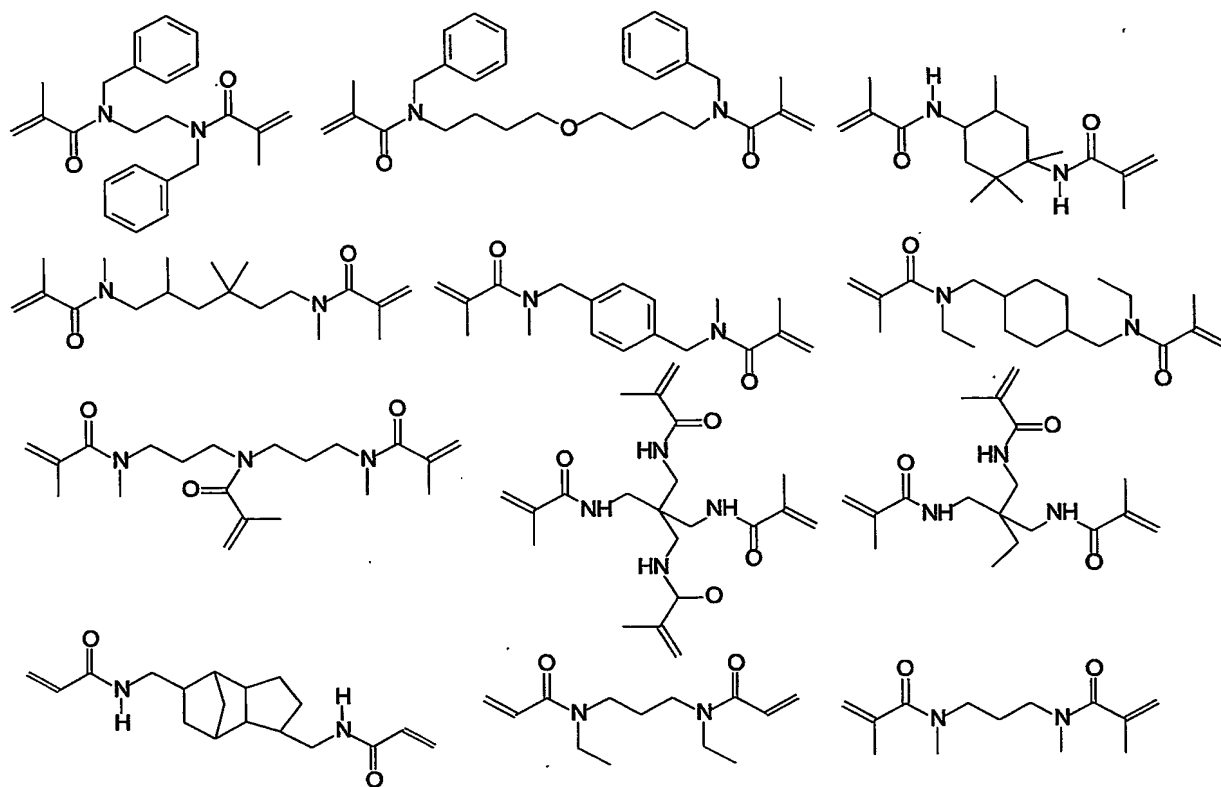
- a divalent substituted or unsubstituted organic residue having from 1 to 45 carbon atoms, whereby said organic residue may contain from 1 to 14 oxygen and/or nitrogen atoms and is selected from a  $C_1$  to  $C_{18}$  alkylene group wherein from 1 to 6  $-CH_2-$  groups may be replaced by a  $-N-(C=O)-CR_9=CH_2$  group wherein  $R_9$  is a hydrogen atom or a  $C_1$  to  $C_{18}$  alkyl group, a divalent substituted or unsubstituted  $C_3$  to  $C_{18}$  cycloalkyl or cycloalkylene group, a divalent substituted or unsubstituted  $C_4$  to  $C_{18}$  aryl or heteroaryl group, a divalent substituted or unsubstituted  $C_5$  to  $C_{18}$  alkylaryl or alkylheteroaryl group, a divalent substituted or unsubstituted  $C_7$  to  $C_{30}$  aralkyl group, and a divalent substituted or unsubstituted  $C_2$  to  $C_{45}$  mono-, di- or polyether group having from 1 to 14 oxygen atoms,

$R_8$  represents

- a saturated di- or multivalent substituted or unsubstituted  $C_2$  to  $C_{18}$  hydrocarbon group, a saturated di- or multivalent substituted or unsubstituted cyclic  $C_3$  to  $C_{18}$  hydrocarbon group, a di- or multivalent substituted or unsubstituted  $C_4$  to  $C_{18}$  aryl or heteroaryl group, a di- or multivalent substituted or unsubstituted  $C_5$  to  $C_{18}$  alkylaryl or alkylheteroaryl group, a di- or multivalent substituted or unsubstituted  $C_7$  to  $C_{30}$  aralkyl group, or a di- or multivalent substituted or unsubstituted  $C_2$  to  $C_{45}$  mono-, di-, or polyether residue having

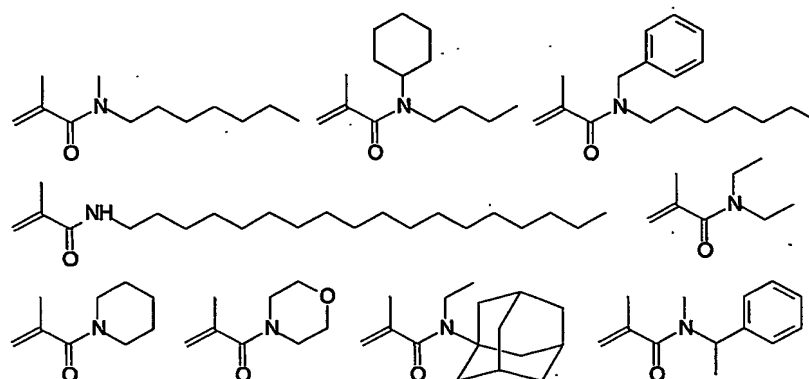
from 1 to 14 oxygen atoms, and  
n is an integer.

11. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said polymerizable monomer is a mono-, bis- or poly(meth) acrylamide characterized by one of the following formulas:





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12. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, which contains said acidic polymerizable monomers of components (a) and (b) in an amount of from 5 to 90 wt-%.
13. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said polymerization initiator is a thermal initiator, a redox-initiator or a photo initiator.
14. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said photo initiator is champhor quinone.
15. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said filler is an inorganic filler and/or an organic filler; preferably the filler is a nanofiller.
16. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said stabilizer is a radical absorbing monomer such as hydroquinone, hydroquinone monomethylether, 2,6-di-tert.-butyl-p-cresol.
17. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein L represents
  - an (a+b)-valent saturated aliphatic C<sub>2</sub> to C<sub>18</sub> group having at least 2 of said primary aliphatic carbon atoms, and optionally 1 or more of said secondary aliphatic carbon atom(s), whereby said (a+b)-valent group may be substituted by C<sub>1</sub> to C<sub>5</sub> alkyl group(s); or
  - a C<sub>2</sub> to C<sub>45</sub> mono-, di-, or polyether which has from 1 to 14 oxygen atoms and

is substituted by at least 2 C<sub>1</sub> to C<sub>10</sub> aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms; whereby said ether may optionally be substituted by C<sub>1</sub> to C<sub>5</sub> alkyl group(s); or

wherein L represents:

a saturated C<sub>3</sub> to C<sub>8</sub> cyclic, C<sub>7</sub> to C<sub>15</sub> bi- or polycyclic hydrocarbon group having from 0 to 4, preferably, 0 to 3, more preferably 0 or 1, of said secondary alicyclic carbon atoms; and/or

a C<sub>4</sub> to C<sub>18</sub> aryl or heteroaryl group having from 0 to 5, preferably 0 to 3, more preferably 0 or 1, of said aromatic carbon atoms; whereby said saturated hydrocarbon or aryl or heteroaryl group is substituted by from 0 to 5 C<sub>1</sub> to C<sub>5</sub> alkyl group(s);

from 0 to 4, preferably 1 to 3, more preferably 1 or 2, saturated C<sub>1</sub> to C<sub>10</sub> aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms, and/or

from 0 to 2 divalent residues according to one of the following formulas:

-[O-CH<sub>2</sub>CH<sub>2</sub>]-<sub>f</sub> wherein f is an integer of from 1 to 10, preferably 1 to 5;

-[O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]-<sub>g</sub> wherein g is an integer of from 1 to 10, preferably 1 to 5;

-[O-R<sub>12</sub>]-<sub>h</sub> wherein R<sub>12</sub> is -CH(CH<sub>3</sub>)-CH<sub>2</sub>- or -CH<sub>2</sub>-CH(CH<sub>3</sub>)- and h is an integer of from 1 to 10, preferably 1 to 5;

-[O-R<sub>14</sub>]-[O-R<sub>15</sub>]- or -[O-R<sub>15</sub>]-[O-R<sub>14</sub>]- wherein R<sub>14</sub> is -CH<sub>2</sub>CH<sub>2</sub>-, R<sub>15</sub> is -CH(CH<sub>3</sub>)-CH<sub>2</sub>- or -CH<sub>2</sub>-CH(CH<sub>3</sub>)-, i, j, k, and l are integers whereby  $2i + 3j \leq 15$  and  $2k + 3l \leq 15$ ,

-[O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]-<sub>r</sub> wherein r is an integer of 1 or 2;

wherein said divalent residues have one of said primary aliphatic carbon atoms; and

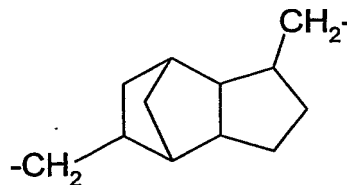
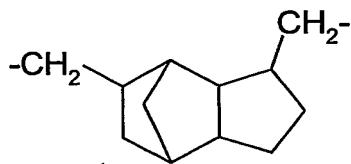
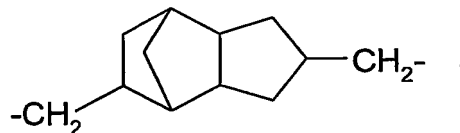
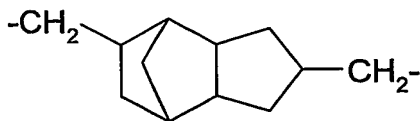
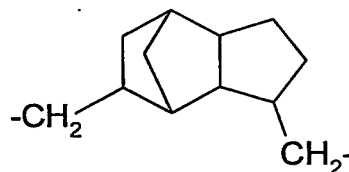
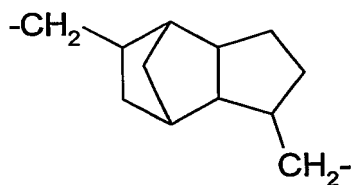
whereby 2 groups selected from said saturated hydrocarbon, aryl, and heteroaryl groups may optionally be linked by a single bond, an alkylene group, or -O-.

18. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein L represents
  - an (a+b)-valent saturated C<sub>3</sub> to C<sub>8</sub> cyclic or C<sub>7</sub> to C<sub>15</sub> bi- or tricyclic hydrocarbon group having at least 2 of said secondary alicyclic carbon atoms;
  - an (a+b)-valent saturated C<sub>4</sub> to C<sub>18</sub> aryl or heteroaryl group having from 2 to 6 of said aromatic carbon atoms;
  - an (a+b)-valent C<sub>6</sub> to C<sub>18</sub> alkylaryl or alkyl heteroaryl group having at least one of said aromatic carbon atoms, at least one of said secondary aliphatic carbon atoms, and

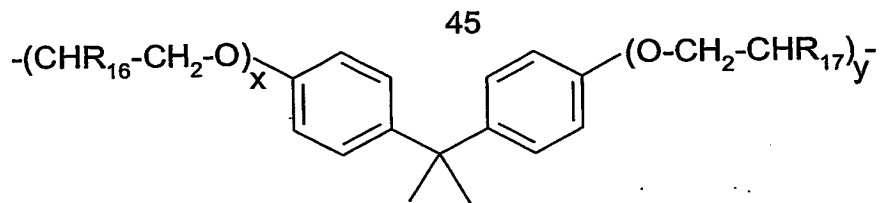
optionally one of said primary aliphatic carbon atoms at the terminal end of the alkyl moiety of said alkylaryl or alkylheteroaryl group; or  
 an (a+b)-valent C<sub>8</sub> to C<sub>30</sub> aralkyl group having at least one of said primary aliphatic carbon atoms and at least one of said secondary aliphatic carbon atoms.

19. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein L represents is a divalent residue according to one of the following formulas:

-[CH<sub>2</sub>CH<sub>2</sub>-O]<sub>m</sub>-CH<sub>2</sub>CH<sub>2</sub>- wherein m is an integer of from 1 to 14,  
 -[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O]<sub>p</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- wherein p is an integer of from 1 to 14,  
 -[R<sub>12</sub>-O]<sub>q</sub>-R<sub>13</sub>- wherein R<sub>12</sub> and R<sub>13</sub> may be -CH(CH<sub>3</sub>)-CH<sub>2</sub>- or -CH<sub>2</sub>-CH(CH<sub>3</sub>)- and q is from 1 to 14,  
 -[R<sub>14</sub>-O]<sub>r</sub>-[R<sub>15</sub>-O]<sub>s</sub>-R<sub>14</sub>- or -[R<sub>14</sub>-O]<sub>t</sub>-[R<sub>15</sub>-O]<sub>u</sub>-R<sub>15</sub>- wherein R<sub>14</sub> is -CH<sub>2</sub>CH<sub>2</sub>-, R<sub>15</sub> is -CH(CH<sub>3</sub>)-CH<sub>2</sub>- or -CH<sub>2</sub>-CH(CH<sub>3</sub>)-, r, s, t, and u are integers whereby 2r + 3s ≤ 43 and 2t + 3u ≤ 42,  
 -[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O]<sub>r</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- wherein r is 1 or 2,

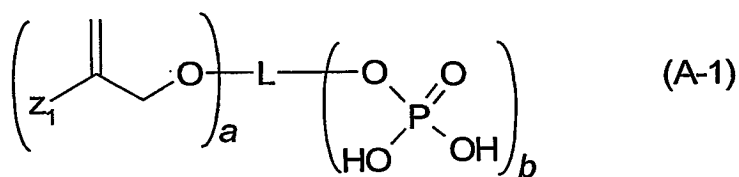


or



wherein  $R_{16}$  and  $R_{17}$  are H or  $-CH_3$  and  $x$  and  $y$  may independently be integers of from 0 to 10, preferably 0 to 5.

20. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said  $(a+b)$  carbon atoms are primary aliphatic carbon atoms.
21. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims wherein the polymerizable acidic phosphoric acid ester monomer is of the following formula (A-1):



wherein

$Z_1$  is  $\text{COOR}^{10}$ ,  $\text{COSR}^{20}$ ,  $\text{CON}(\text{R}^{10})_2$ ,  $\text{CONR}^{10}\text{R}^{20}$ , or  $\text{CONHR}^{10}$ , wherein  $\text{R}^{10}$  and  $\text{R}^{20}$  independently represent

- a hydrogen atom,
- a  $\text{C}_{1-18}$  alkyl group optionally substituted by a  $\text{C}_{3-8}$  cycloalkyl group,
- an optionally substituted  $\text{C}_{3-8}$  cycloalkyl group,
- an optionally substituted  $\text{C}_{4-18}$  aryl or heteroaryl group,
- an optionally substituted  $\text{C}_{5-18}$  alkylaryl or alkylheteroaryl group, or
- an optionally substituted  $\text{C}_{7-30}$  aralkyl group,

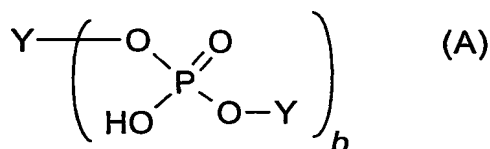
whereby two  $\text{R}_1$  residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms, and whereby the optionally substituted groups may be substituted by 1 to 5  $\text{C}_{1-5}$  alkyl group(s);

L represents an  $(a+b)$ -valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including  $a + b$  carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said  $a+b$  carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

$a$  is an integer of from 1 to 10, preferably 1 to 5;

$b$  is an integer of from 1 to 10, preferably 1 to 5.

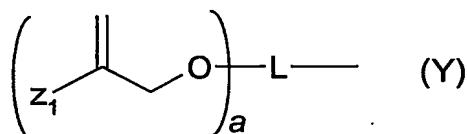
22. The one-part self-etching, self-priming dental adhesive composition according to any one of claims 1 to 20 wherein none of the moieties Y is a hydrogen atom.
23. A polymerizable acidic phosphoric acid ester monomer of the following formula (A)



wherein

the moieties Y independent from each other represent

a moiety of the following formula (Y)



wherein

$Z_1$  is  $\text{COOR}^{10}$ ,  $\text{COSR}^{20}$ ,  $\text{CON}(\text{R}^{10})_2$ ,  $\text{CONR}^{10}\text{R}^{20}$ , or  $\text{CONHR}^{10}$ , wherein  $\text{R}^{10}$  and  $\text{R}^{20}$  independently represent

a hydrogen atom,

a  $\text{C}_{1-18}$  alkyl group optionally substituted by a  $\text{C}_{3-8}$  cycloalkyl group,

an optionally substituted  $\text{C}_{3-8}$  cycloalkyl group,

an optionally substituted  $\text{C}_{4-18}$  aryl or heteroaryl group,

an optionally substituted  $\text{C}_{5-18}$  alkylaryl or alkylheteroaryl group, or

an optionally substituted  $\text{C}_{7-30}$  aralkyl group,

whereby two  $\text{R}_1$  residues may form together with the adjacent nitrogen atom to which they are bound a 5- to

7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,  
and whereby the optionally substituted groups may be substituted by 1 to 5 C<sub>1-5</sub> alkyl group(s);

L represents an (a+b)-valent organic residue (whereby b is 1 when Y in formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5, more preferably 1.